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## MACHINE TRANSLATION: ITS PAST, PRESENT AND FUTURE

### I. Why should we have Machine Translation?

One of the great concerns of American science is how to keep up with the scientific accomplishments in countries where language barriers may prevent the direct evaluation of the scientific literature. American scientists are not known for their linguistic prowess, so they must depend on those few qualified linguist-scientists to interpret foreign language materials into usable form. In the case of the Russian language materials, the output of scientific writing amounts to 300,000,000 words per year. The distribution of these words is as follows:

Chemistry	26,000,000	words/year
Physico-Mathematical Sciences	80,000,000	words/year
Biosciences	41,000,000	words/year
Geology and Geography	17,000,000	words/year (journal articles only)
Other sciences	136,000,000	words/year

The above cited statistics were accumulated from the 1958 issues of KNIZHNAYA LETOPIS' (Book Annals) and LETOPIS' ZHURNAL'NYKH STATEI (Annals of Journal Articles). One is shocked by the fact that less than 2% of the current Russian technical output is now being exploited in any way, i.e., translated, abstracted, extracted or summarized. With the removal of the burden of translation chores from the shoulders of the limited reservoir of technical linguists in the United States by the operational capability of machine translation, the time now spent in this endeavor can be re-allocated to scanning of almost the total Russian language output to identify what is worth translating then turning the actual translation problem over to the machine. When we realize that the average technical linguist can translate only about 2600 words a day and the machine can and has handled 3400 words in 6 minutes (translation from French to English), the potentiality for machine translation becomes obvious.

A concomitant benefit to the United States which cannot be easily evaluated will be the elimination of the excuse of the American scientist that he needn't bother looking at the Russian language material because he can't read it anyway, and if he does look at the abstracting journals and identifies an interesting paper, he will have to wait months to get a translation made.

### II. History of Machine Translation:

The first known references to the translation of natural languages by machine were in the patents granted to P. P. Troyanskii by the USSR in

1933. These patents refer to an automatic dictionary which was never reduced to practice. Shortly after World War II an exchange of correspondence took place between Warren Weaver and Andrew Booth, the essence of which was -- wouldn't it be nice if we could translate mechanically. In 1952 a meeting of linguists, logicians and mathematicians was held at MIT on the subject of machine translation. The principal result of that meeting was the stimulation of interest and the realization of possibility in the minds of such eminent linguists as Prof. Leon E. Dostert of Georgetown University. Prof. Dostert set to work with a minimum of financial support and the cooperation of IBM to see whether the proposition was feasible. In January 1954 he demonstrated for the first time in history the fact that translation by machine was possible. His demonstration was limited by a vocabulary of 250 words and six linguistic rules. After several frustrating experiences in attempting to interest agencies of government in his system, Prof. Dostert received a grant from the Central Intelligence Agency and the National Science Foundation in June 1956. Up until June 1959 these two agencies supported Prof. Dostert's work. At that time the National Science Foundation decided that the direction of the work was being thrust too heavily toward operational capability and not enough toward research in linguistics. It was therefore inappropriate for the Foundation to continue to support this work. The CIA had an urgent need for operational capability so the orientation of the entire project was directed toward an early production of translation by machine. The processing of 500,000 words of the Russian language literature of organic chemistry resulted in a vocabulary of almost 12,000 words - sufficient to undertake random translation of texts in the discipline mentioned. Routines for the accumulation of vocabularies in any desired discipline were set up. The work in the translation of French language materials in physics had simultaneously reached production possibilities. Thus, for the next grant period it was decided to undertake the translation of 30,000,000 words of Russian scientific literature to establish empirically whether full-scale production was feasible. It is at this point that the project now stands.

### III. The Present Situation:

In the machine translation projects sponsored by the research components of the military services and the National Science Foundation, the work may be categorized into three groups. Some of the principal researchers have stated publicly that they are doing research in linguistics without the immediate aim of accomplishing production translations. Another group of research centers is concentrating on word-for-word translation without concern for the information bearing content of syntactic structure. A third group concerns itself with the construction of special machines for translation or the input to a machine translator (automatic reading falls into this latter category). The total commitment for funds is difficult to pin down, but according to the reported figures applicable to machine translation research exclusive of the work on reading machines but including the work on translating machines, the amount for Fiscal Year 1960 is approximately \$2,000,000. The monies spent over the past three fiscal years will average about \$1,750,000 per year. It

seems to us that with this amount spent, the government should now establish whether large-scale production is feasible. If it is so established, and we are certain it will be, the coordination of continued research will become easier and more meaningful. There is no question but what the United States must continue research in all scientific fields if it is to sustain a pre-eminent place in the world. Machine Translation is no exception. We sincerely hope that the results of the CIA-Georgetown University attempt to go into production of translations by machine will not be taken to mean that the problem is completely solved and no further research will be necessary. Our firm conviction is that one of the several research projects in the field must prove operational feasibility now, and since the Georgetown project is generally acknowledged to be the furthest toward that goal, we are prepared to carry out the final step of proof.

There is more concern over whether this step should be taken than is warranted. Some people have said that if we prove operational capability, the research money will dry up. We question the motives of such people toward their research work. Our contention is that unless such a proposition is carried through, the research is in jeopardy.

#### IV. What about the quality of machine output?

The quality of any product is the acceptance that that product has by its consumers. There has been argument among the various centers of research in machine translation as to who shall say when a machine output is acceptable. All of the researchers are striving for as near perfect a product as possible. But we submit that the greatest enemy of progress is perfection. If the first approximation in production-level machine translation is acceptable to the people who are in need of such translations, we believe that we have a useful product. Attached to this paper are samples of machine translation of a text selected at random and processed by Georgetown University. Comparison between the actual machine output and a cursory editing, or as we prefer to call it, revising job and a translation of the same article made by a human translator manifestly demonstrates the quality to be expected.

There are some who refuse to accept the machine product as a "translation" and refer to the final revision as machine-aided, human-postedited translation. By the same token then translations now produced commercially and in the translation centers of government should be called human-translated, human-postedited translations, the quality of information transfer in which is very considerably below the machine product. No amount of argument on our part will ever settle the point, however.

#### V. What about the future of machine translation?

As may be induced from the above recitation, we believe in machine translation as an instrument in the understanding of scientific progress in the world without the sacrifice of linguistic integrity. The Director of Central Intelligence, Mr. Allen W. Dulles, in a letter

to the Director of the National Science Foundation dated 29 February 1956, said,

"It is our opinion that much is to be gained by the early development of a machine capability for translation. The National Security can be well served if we have available the scientific and technical literature of the USSR in English for detailed analysis as early after publication as possible. ....

"The objective of this research would have as its primary aim the resolution of accurate lexical transfer between the source language and the target language and the development of a method for syntactic rearrangement in accordance with the requirements of the structure of the target language. We are sure that the addition to our understanding of language and syntax will be a bonus effect."

Everything which Mr. Dulles said in this letter written four years ago has proven to be accurate. Much of the concern which the American people had over the scientific achievements of the USSR could have been prevented had they known of the direction of research in chemistry, astronautics and communications contained in the openly published literature of the USSR. Some of the concern was false and generated by headline seeking journalists or pseudo-scientists, but the point remains valid that if the American people had available the scientific literature of the USSR in understandable form, the accomplishments of Soviet science would not have been as alarming because we would have known of the direction of the research and the probable imminence of success. Necessary counteractions would have been taken by instituting research programs in the United States to anticipate or predate the same successes.

The future of machine translation suggests a center to be operated by the government or on behalf of the government where rapid, accurate translation of materials from foreign languages to English can be accomplished. One suggestion for the future might be the establishment of a National Institute of Language Sciences using the National Institutes of Health as the model. Such an organization could deal with all the problems associated with human communication. Divisions in the Institute would attack the problems of mechanical linguistics, pedagogical linguistics, cultural linguistics, psychological linguistics and lexicology.

The Division of Mechanical Linguistics would handle the problems of machine translation, language data processing for storage and retrieval of information, machine abstracting, oral language interpretation by machine, and mathematical linguistics. The Division of Pedagogical Linguistics would be concerned with the methodology of language teaching, the preparation of teaching materials for the less usual languages, the problem of a meta-language (or common language), and the maintenance of language research centers abroad. The Division of Cultural Linguistics would have as its goal the establishment of methods of inter-cultural communication, literacy programs, cultural semantics, and emerging

language problems. In Psychological Linguistics would be studied the relationships between language and motivation, language and mental derangements, language and moral values, and the psychology of language learning. The last division would be concerned with lexicology with particular emphasis on the collation of scientific and technical terminologies. For further development of this idea, we refer you to Prof. Leon E. Dostert whose original concept it is.

In summary then, we believe that machine translation will become the usual method of transference of ideas from one culture to another. It is now going through some of the same types of scepticism which simultaneous interpretation went through 15 years ago. Since the leading proponent of both of these radical methods of language processing was the same man, Prof. Dostert, the probability of success in machine translation is the same as has been demonstrated with simultaneous interpretation.

Annex A

Machine Translation of Russian  
to English

The attached appendices were made from a randomly selected article from the Journal of General Chemistry published in the Soviet Union.

- Appendix 1 - The original Russian article.
- Appendix 2 - The actual machine output.
- Appendix 3 - The revised machine output as we would expect to publish such products.
- Appendix 4 - The control translation for comparison with the machine output.

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КАТАЛИТИЧЕСКОЕ АЛКИЛИРОВАНИЕ ФЕНОЛА  
МЕТИЛОВЫМ СПИРТОМ

И. Н. Самсонова

Каталитическому алкилированию фенола вторичными и третичными спиртами посвящен ряд работ [1-8]. Попытки каталитического алкилирования фенола первичными спиртами привели к отрицательным результатам [2, 9] или сопровождалась незначительными выходами [10-12]. При алкилировании фенола метиловым спиртом наилучшие результаты были получены на активированной окиси алюминия [1].

Нами был изучен процесс алкилирования фенола метиловым спиртом над активированным природным алюмосиликатным катализатором — глиной гумбрин при атмосферном давлении в обычной установке, применяемой при исследовании парофазных каталитических реакций в проточной системе. В результате реакции были получены жидкие и газообразные продукты. Жидкий двухслойный конденсат, помимо не вошедших в реакцию исходных веществ, содержал воду, алкилирующие фенолы и нейтральные продукты реакции.

Для выяснения зависимости выхода алкилирующих продуктов от температуры накопление конденсата для анализа производилось при трех температурах (350, 420 и 500 °), при молярном соотношении фенола и метилового спирта 1:6 и скорости подачи исходной смеси, равной 8-10 мл в час над 100 мг катализатора. С увеличением температуры

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реакции от 350 до 500° выход алкилированных фенолов возрастал почти в 3 раза и достигал 68% (в расчете на фенолы конденсата). Оптимальный выход нейтральных продуктов конденсации был получен при 420° и составлял 23% (в расчете на весь конденсат).

Алкилированные фенолы, полученные при трех исследуемых температурах, представляли собой смесь производных фенола, содержащую крезолы, ксиленолы и более сложные продукты. Количество последних заметно возрастало с увеличением температуры реакции. Смесь алкилированных фенолов, полученная при 350°, содержала 32% о-крезола. В продуктах алкилирования, полученных при 420°, установлено присутствие о- и м-крезола. Из фенольной части конденсата, полученного при 500°, выделено незначительное количество о-крезола и 3,5-диметилфенола. Основная масса фенолов, полученных при этой температуре, состояла из высококипящих сложных продуктов алкилирования.

В нейтральной части конденсатов, помимо спирта и воды, обнаружены анизол, о-метиланизол и гексаметилабензол. В наибольшем количестве (60,8% в расчете на нейтральное масло) анизол был получен при 420°. Максимальный выход гексаметилабензола (14%) получается при 500°. Количество о-метиланизола во всех случаях незначительное.

#### ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

В результате каталитической конденсации фенола с метиловым спиртом над активированной соляной кислотой глиной-гумбрином получены двуслойные конденсаты. Водный и масляный слои разделялись, от каждого слоя отгонялся продукт, кипящий до 100°. Маслянистый остаток, кипящий выше 100°, многократно экстрагировался 10% NaOH. Полученные фенолаты извлекались эфиром для освобождения от частично увлеченных щелочью нейтральных масел и разлагались разбавленной H<sub>2</sub>SO<sub>4</sub>.

После высушивания эфирного раствора и удаления эфира получалась смесь фенолов, которая затем подвергалась фракционированию. До 182° отгонялся непрореагировавший фенол. Далее на колонке фракционировались производные фенола. Фенолы анализировались методом арилирования<sup>[15]</sup>. Полученные кристаллические арилгликолевые кислоты разделялись дробной кристаллизацией.

В процессе работы было установлено, что катализатор после 18-часовой работы терял свою активность почти на 30%. Такая дезактивация катализатора вызывается, вероятно, отложениями смолистых остатков и угля на его поверхности, в результате чего поверхность катализатора становится недоступной для реагирующих веществ. Во всех опытах после 6-часовой работы катализатор регенерировался путем продувания через реакционную трубку воздуха при температуре 350°. После 18-часовой работы в реакционную трубку помещалась свежая порция катализатора.

Исходными веществами служили свежесинтезированный высушенный фенол и перегнанный метиловый спирт.

Алкилирование при 350°. Исходная смесь: 365,4 г фенола, 746 г метилового спирта. После отделения нейтральных продуктов и неспециального фенола получено 38 г фенольного продукта с т. кип. 182–210° и 159 г нейтрального масла, кипящего в границах 152–250°. В результате фракционирования на колонке из фенольной смеси выделено 11,5 г фракции с т. кип. 187–189°. Полученная из части фракции арилгликолевая кислота после перекристаллизации имела т. плав. 151–152°, что соответствует температуре плавления о-крезоксиуксусной кислоты (по литературным данным, 152°).

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1) Анизол (48.5 г): т. кип. 155°,  $n_D^{20}$  1.5162,  $d_4^{20}$  0.9884.

Найдено:  $M$  108, 109.5.  $C_7H_8O$ . Вычислено:  $M$  108.

2) *o*-Метиланизол (11 г): т. кип. 170—172°,  $n_D^{20}$  1.5190,  $d_4^{20}$  0.9850.

Найдено:  $M$  122, 125.  $C_8H_{10}O$ . Вычислено:  $M$  122.

3) Гексаметилбензол (4.8 г) — длинные иглы, т. пл. 164—166° (по литературным данным, 166°).

Найдено:  $M$  161, 165.  $C_{12}H_{18}$ . Вычислено:  $M$  162.

Газообразные продукты реакции содержали 12.4%  $H_2$ , 32%  $CO_2$ , 10.8%  $CO$ , 9.2%  $C_2H_6$ .

Алкилирование при 420°. Исходная смесь: 305 г фенола, 623 г метилового спирта. После отделения нейтральных продуктов и неизмененного фенола получено 36 г фенольной смеси с т. кип. 182—224°. В результате фракционирования смеси выделены две фракции, в которых доказано присутствие изомерных крезолов. Фракция 189—191° (6 г) содержала *o*-крезол. Температура плавления полученной ариллагиколовой кислоты 151—152° (по литературным данным, 152°). Фракция 200—203° (2.8 г) содержала *m*-крезол. Температура плавления ариллагиколовой кислоты 100—103°, что соответствует температуре плавления *m*-крезоксисукусной кислоты (по литературным данным, 103°).

Исследование нейтрального масла (128 г) показало, что в нем содержится анизол (62 г), *o*-метиланизол (7.5 г) и гексаметилбензол (7 г).

Алкилирование при 500°. Исходная смесь: 305 г фенола, 623 г метилового спирта. После предварительной обработки конденсата получено 105.5 г смеси алкилированных производных фенола с т. кип. 182—233° и 12 г фенолов с т. кип. выше 233°. В результате анализа фенольной смеси было установлено присутствие незначительного количества *o*-крезола (температура плавления полученной *o*-крезоксисукусной кислоты 151—152°) и 3,5-диметилфенола (температура плавления полученной ариллагиколовой кислоты 84—86°).

Нейтральное масло (88 г) содержало анизол (28.5 г), *o*-метиланизол (7 г) и гексаметилбензол (14.2 г).

#### Выводы

Смесь метилового спирта с фенолом при 320—500° над природным алюмосиликатным катализатором — глиной-гумбрином образует алкилированные производные фенола и нейтральные продукты. Выделены *o*- и *m*-крезол и 3,5-диметилфенол. Нейтральные продукты реакции содержат анизол, *o*-метиланизол и гексаметилбензол.

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THUS, IN FACT REVERSIBLE OF A REACTION, THERE ARE SUCH IN ALL RANGE OF TEMPERATURES, UNDER WHICH IN GENERAL CAN EXIST THE IN QUESTION SUBSTANCES. PRACTICALLY HOWEVER REVERSIBILITY WAS NOTED ONLY IN CERTAIN A MORE IN RANGE, FOR EXAMPLE FOR THE REACTION OF THE FORMATION WATER / UNDER THE USUAL PRESSURE / BETWEEN 2000 AND 4000at.

[illegible]

T. N. A. SATHISUNO

TO THE CATALYTIC ALKYLATION OF PHENOL SPECIFICALLY WITH ETHYL ALCOHOL. WE REPORTED A SERIES OF WORKS (1-4). THE EFFECTS OF A VARIOUS NUMBER OF SUBSTITUENTS BY ALCOHOLS LED TO NEGATIVE RESULTS (2,3,6) ON THE OTHER HAND INSTANTANEOUS YIELDS (10 - 12% UPON THE ALKYLATION OF PHENOL) BEST RESULTS WERE OBTAINED ON THE ALKYLATION OF PHENOL WITH

BY US WAS STUDIED THE PROCESS OF THE ALKYLATION OF THE PRIMARY ALCOHOL OVER ACTIVATED NATURAL ALKALICALLY BY A CATALYST -  $\text{Fe}(\text{CO})_5$  AT ATMOSPHERIC PRESSURE IN THE USUAL APPARATUS, APPLIED ALSO THE REACTION OF VAPOR-PHASE CATALYTIC REACTIONS IN A CIRCULATING SYSTEM AND A CATALYST REACTION WERE OBTAINED LIQUID AND GASEOUS PRODUCTS. A LIQUID FRACTIONATED

CONDENSATE, BESIDES NOT WHICH DID NOT ENTER INTO THE REACTION OF THE INITIAL SUBSTANCES, CONTAINED WATER, ALKYLATED PHENOLS AND NEUTRAL THE REACTION PRODUCTS.

FOR VYASNEVIA THE RELATIONS OF THE YIELD OF THE ALKYLATED PRODUCTS FROM TWO TEMPERATURES, THE ACCUMULATION OF A CONDENSATE FOR ANALYSIS WERE CARRIED OUT AT TWO TEMPERATURES 70°C AND 500°C, UPON THE MOLAR RATIO OF THE REACTANTS IN A NEUTRAL ALCOHOL 1:1 FOR OF THE SUPPLY OF THE INITIAL MIXTURE, EQUAL 6-10 ML. INTO A HOUR OVER 100 ML. OF A CATALYST. WITH AN INCREASE OF THE REACTION TEMPERATURE FROM 350 TO 500°C THE YIELD OF THE ALKYLATED PHENOLS INCREASED ALMOST IN A OF A TIME AND AMOUNTED TO 68% IN A ESTIMATE ON THE PHENOLS OF A CONDENSATE/. THE OPTIMUM YIELD OF THE NEUTRAL PRODUCTS OF CONDENSATION WAS OBTAINED AT 420°C AND CONSISTED 23% IN A ESTIMATE ON ALL THE CONDENSATE/.

ALKYLATED PHENOLS, WHICH WERE OBTAINED UPON THE THREE STUDIED TEMPERATURES, REPRESENTED A MIXTURE OF DERIVATIVES OF BENZOL, OF TOLUOL, OF CRESOL, OF XYLENOL, OF NITROBENZOL AND MOST COMPLEX PRODUCTS. A ANALYSIS OF THE MIXTURE INDICATEDLY INCREASED WITH AN INCREASE OF THE REACTION TEMPERATURE. A MIXTURE OF ALKYLATED PHENOLS, OBTAINED AT 350°C, CONTAINED 92% CRESOL. IN THE PRODUCTS OF THE ALKYLATION, OBTAINED AT 420°C, IT IS ESTABLISHED THE PRESENCE OF C- AND M-XYLENOL. FROM ANALYTIC DATA OF A CONDENSATE, OBTAINED AT 500°C, IT IS ISOLATED AN INDISTINGUISHABLE MIXTURE OF THE ALKYLATED 2,6-DIMETHYLBENZOL. THE BASIC MASS OF THE PHENOLS, WHICH WERE OBTAINED AT THIS TEMPERATURE, CONSISTED FROM THE MONOMOLAR COMPLEX PRODUCTS OF THE ALKYLATION.

IN NEUTRAL PARTS OF CONDENSATES, BESIDES ALCOHOL OBSERVABLE, DISCOVERED ANISOL, O-METILANIZOL AND A HEXAMETHYLENE. IN A MIXTURE QUANTITY 70.8% IN A ESTIMATE ON A NEUTRAL OIL/A ANALYSIS WAS OBTAINED AT 70°C. THE MAXIMUM YIELD OF THE HEXAMETHYLENE (14%) IS OBTAINED AT 500°C. AN

AMOUNT O-METILANIZOLA IN ALL CASES INSIGNIFICANT.

#### AN EXPERIMENTAL PART

AS A RESULT OF CATALYTIC CONDENSATION WITH METHYL ALCOHOL OVER ACTIVATED HYDROCHLORIC ACID BY A GUMBRIN CLAY THEY ARE OBTAINED TWO-LAYERED CONDENSATES. AQUEOUS AND OILY LAYERS RAZDEL4LI. FROM EACH LAYER THERE WAS DISTILLED A PRODUCT, WHICH BOILS UP TO 100°. THE OILY RESIDUE, WHICH BOILS ABOVE 100°, REPEATED WERE EXTRACTED 10% NaOH. OBTAINED PHENOLATES WERE EXTRACTED WITH ETHER FOR LIBERATION FROM PARTIALLY INVOLVED BY THE ALKALI OF NEUTRAL OILS AND DECOMPOSED DILUTED H<sub>2</sub>SO<sub>4</sub>.

AFTER THE DRYING OF AN ETHER SOLUTION AND THE REMOVAL OF THE ESTER THERE WAS OBTAINED A MIXTURE OF PHENOLS, WHICH THEN WAS SUBJECTED TO FRACTIONATION. UP TO 102° THERE WAS DISTILLED NON-REACTED PHENOL. FURTHER THROUGH A COLUMN THERE WERE FRACTIONATED DERIVATIVE OF PHENOL. PHENOLS WERE ANALYZED BY A METHOD ARUTYOVANIA //15//. OBTAINED CRYSTALLINE DRYGLYCOLIC ACIDS WERE FURTHER FRACTIONAL BY CRYSTALLIZATION.

IN THE PROCESS OF WORK WAS ESTABLISHED, THAT A CATALYST AFTER 15-20 WORKS LOST ITS ACTIVITY ALMOST ON 80%. SUCH DEACTIVATION OF A CATALYST IS CAUSED, PROBABLY, BY THE DEPOSITS OF THE TARRY RESIDUES AND COAL ON ITS SURFACE, AS A RESULT WHICH THE SURFACE OF A CATALYST BECOMES INACCESSIBLE FOR REACTING SUBSTANCES. IN ALL EXPERIMENTS AFTER O-CASOVUI WORK A CATALYST WAS DEGENERATED BY BY MEANS OF PURGING THROUGH THE REACTION TUBE OF AIR AT A TEMPERATURE 350°. AFTER 18-CASOVUI OF WORK INTO A REACTION TUBE WAS PLACED THE FRESH PORTION OF A CATALYST.

BY THE INITIAL SUBSTANCES THERE SERVED FRESHLY DISTILLED DRIED PHENOL AND DISTILLED METHYL ALCOHOL.

A ALKYLATION AT 350°. THE INITIAL MIXTURE.. 365.4 G OF PHENOL, 740 G OF METHYL ALCOHOL. AFTER THE SEPARATION OF THE NEUTRAL PRODUCTS AND UNCHANGED

PHENOL WERE OBTAINED 38 G OF PHENOLIC PRODUCT WITH T. BOILING 182 - 210 AND 159 G OF A NEUTRAL OIL, WHICH ROLLS IN BOUNDARIES 152 - 250°. AS A RESULT OF FRACTIONATION THROUGH A COLUMN FROM A PHENOLIC MIXTURE WERE ISOLATED 11.5 G OF A FRACTION WITH T. BOILING 187 - 189°. OBTAINED FROM PARTS OF A FRACTION A ARYLGLYCOLIC ACID AFTER RECRYSTALLIZATION THERE D T. M. 151 - 152°, THAT IT CORRESPOND THE TEMPERATURE OF THE MELTING O-KREZOKSIUKSUSNOL OF ACID /ACCORDING TO LITERATURE GIVEN, 152°/.

FROM A NEUTRAL OIL, ISOLATED..

1/ A ANISOLE /48.5 G/.. T. BOILING 135°, SN/2/0SD 1.2152, SD/2/0SD 0.9834

FOUND.. M 108, 109.5 • C<sub>17</sub>H<sub>18</sub>O. CALCULATED.. 108.

2/ O-METHYLANIZOL /11 G/.. T. BOILING 179 - 172°, SN/2/0SD 1.2150,

SD/2/0SD 0.985°.

FOUND.. M 122, 125 • C<sub>8</sub>H<sub>10</sub>O. CALCULATED.. M 122.

3/ A HEXAMETHYLENENE /4.8 G/ - LONG NEEDLES, T. M. 154 - 155°

/ACCORDING TO LITERATURE GIVEN, 166°/.

FOUND.. M 161, 165 • C<sub>12</sub>H<sub>18</sub>S. CALCULATED.. M IT IS.

CASEOUS THE REACTION PRODUCTS CONTAINED 12.4% -#2, 33.0% CO#2, 11.3% CO

CO, 5.2 G/3 C<sub>8</sub>H<sub>10</sub>S<sub>2</sub>PH.

A ALKYLATION AT 420°. THE INITIAL MIXTURE.. 502 G OF ANISOL, 523 G OF METHYL ALCOHOL. AFTER THE SEPARATION OF THE NEUTRAL PRODUCTS AND OBTAINED PHENOL WERE OBTAINED 36 G OF A PHENOLIC MIXTURE WITH T. BOILING 182 - 189°. AS A RESULT OF THE FRACTIONATION OF A MIXTURE, THEY ARE ISOLATED TWO OF A FRACTION, IN WHICH WAS SHOWN THE PRESENCE ISOMERIC RESOLLY. A FRACTION 189 - 191° /6 G/ CONTAINED THE O-CRESOL. THE MELTING POINT M OF THE OBTAINED ARYLGLYCOLIC ACID 151 - 152° /ACCORDING TO LITERATURE GIVEN, 152°/. A FRACTION 200 - 203° /2.8 G/ CONTAINED N-KREZOL. THE MELTING POINT OF THE

ARYLGLYCOLIC ACID 100 - 103°, WHICH CORRESPOND THE TEMPERATURE OF THE MELTING OF A M-CRESOXYACETIC ACID /ACCORDING TO LITERATURE GIVEN, 103°/.  
 THE INVESTIGATION OF A NEUTRAL OIL /128 G/ SHOWED, THAT IN A IT

SOLVED ITS A ANISOLE /62 G/, O-METILANIZOL /7.8 G/ AND A HEXAMETHYLBENZENE /7 G/.

A ALKYLATION AT 500°. THE INITIAL MIXTURE.. 305 G OF PHENOL, 623 G OF METHYL ALCOHOL. AFTER THE PREVIOUS TREATMENT OF THE CONDENSATE WERE OBTAINED 105.5 G OF A MIXTURE ALKYLATED DERIVATIVE OF PHENOL WITH T. BOILING 182 - 233° AND 12 G OF PHENOLS WITH T. BOILING ABOVE 233°. AS A RESULT OF THE ANALYSIS OF A PHENOLIC MIXTURE WAS ESTABLISHED THE PRESENCE OF AN INSIGNIFICANT AMOUNT OF A O-CRESOL /THE MELTING POINT WHICH WAS OBTAINED O-KREZOKSIUKSUSNOI ACIDS 151 - 152°/ AND OF A 3,5-DIMETHYLPHENOL /THE MELTING POINT W OF THE OBTAINED ARYLGLYCOLIC ACID 84 - 86°/.

A NEUTRAL OIL /88 G/ CONTAINED A ANISOLE /28.5 G/, O-METILANIZOL /7 G/ AND A HEXAMETHYLBENZENE /14.2 G/.

#### CONCLUSIONS

A MIXTURE OF METHYL ALCOHOL WITH PHENOL AT 320 - 500° OVER A NATURAL ALUMOSILICATE CATALYST - BY A GUMBRIN CLAY IT FORMS ALKYLATED DERIVATIVE OF PHENOL AND NEUTRAL PRODUCTS. WERE ISOLATED O- AND M-KREZOL AND A 3,5-DIMETHYLPHENOL. NEUTRAL THE REACTION PRODUCTS CONTAIN THE ANISOLE, O-METILANIZOL AND A HEXAMETHYLBENZENE.

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The Catalytic Alkylation of Phenol  
by Methyl Alcohol

I. N. Samsonov

Machine Translation revised by Paul W. Howerton

A series of works was dedicated to the catalytic alkylation of phenol by secondary and tertiary alcohols (1-8). Attempts of catalytic alkylation of phenol by alcohols led to negative results (2,3,9) or they were accompanied by insignificant yields (10-13). For the alkylation of phenol by methyl alcohol, best results were obtained on the activated oxides of aluminum (14).

We studied the process of alkylation of phenol by methyl alcohol over activated natural aluminosilicate as catalyst - gumbrin clay - at atmospheric pressure in the usual apparatus used for the investigation of vapor phase catalytic reactions in a circulating system. As a result of the reaction, there were obtained liquid and gaseous products. A two-layered liquid condensate, besides the starting substances which did not enter into the reaction, contained water, alkylated phenols and neutral reaction products.

For clarification of the relations of the yield of the alkylated products with temperature, an accumulation of condensate for analysis was carried out at 3 temperatures (350, 420, and 500°), at a molar ration of phenol to methyl alcohol of 1-6, and at a feed rate of the initial mixture equal to 8-10 ml. per hour over 100 ml. of the catalyst. With an increase of reaction temperature from 350 to 500°, the yield of the alkylated phenols increased almost 3 times and amounted to 68% (based on the phenols in the condensate). The highest yield of the neutral condensation products was obtained at 420° and constituted 23% (based on total condensate).

Alkylated phenols, which were obtained at the 3 temperatures, represented a mixture of derivatives of phenol containing cresols, xylenols and more complex products. The amount of the latter noticeably increased with an increase in reaction temperature. A mixture of alkylated phenols obtained at 350° contained 32% o-cresol. From the products of the alkylation obtained at 420°, the presence of o- and m-cresol was established. From the phenolic parts of the condensate obtained at 500°, an insignificant amount of o-cresol and 3,5-dimethylphenol was isolated. The basic mass of the phenols, which was obtained at this temperature, consisted of the high-boiling complex products of the alkylation.

In the neutral parts of the condensates, besides alcohol, anisole, o-methylanisole and hexamethylbenzene were discovered. The maximum quantity (60.8%-based on the neutral oil) of anisole was obtained at 420°. The maximum yield of the hexamethylbenzene (14%) is obtained at 500°. The amount of o-methylanisole was in all cases insignificant.

#### The Experimental Part

As a result of catalytic condensation of phenol with methyl alcohol over gumbrin clay activated by hydrochloric acid, two-layered condensates were obtained. The aqueous and oily layers were separated and from each layer a product was distilled which boils up to 100°. The oily residues which boil above 100° were extracted repeatedly with 10% NaOH. The obtained phenolates were extracted with ether for liberation from neutral oils partially occluded by the alkali and washed with dilute  $H_2SO_4$ .

After drying the ether solution and removal of the ether, there was obtained a mixture of phenols which then was subjected to fractionation.

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Up to 182° the non-reacted phenol was distilled. Then the derivatives of phenol were fractionated. The phenols were analyzed by the arylation method (15). The obtained crystalline arylglycolic acids were separated by fractional crystallization.

In the course of the work, it was established that a catalyst after 18 hours of operation lost almost 30% of its activity. Such deactivation of a catalyst is probably caused by the deposits of the tarry residues and carbon on its surface; as a result of which the catalyst becomes inaccessible to the reacting substances. In all experiments, after 6 hours of operation, the catalyst was regenerated by blowing air through the reaction tube at 350°. After 18 hours of operation, a fresh portion of catalyst was placed into the reaction tube.

As starting materials, freshly distilled, dried phenol and distilled methyl alcohol were used.

Alkylation at 350°. The initial mixture...365.4 g. of phenol, 746 g. of methyl alcohol. After the separation of the neutral products and unchanged phenol, 38 g. of phenolic product were obtained with b.p. 182-210° and 159 g. of a neutral oil which boils between 152-250°. As a result of fractionation from the phenolic mixture 11.5 g. of a fraction were isolated with b.p. 187-189°. Arylglycolic acid was obtained from parts of the fraction after recrystallization with m.p. 151-152° which corresponds to the m.p. of o-cresoxyacetic acid (according to the literature - 152°).

From the neutral oil there were isolated:

1) Anisole (48.5 g.)..b.p. 155°,  $n_D^{20}$  1.5162,  $d_4^{20}$  0.9884

Found M.W. 108, 109.5.  $C_7H_8O$ . Calculated M.W. 108

2) o-Methylanisole (11 g.)..b.p. 170-172°,  $n_D^{20}$  1.5190,  $d_4^{20}$  0.9850

Found M. W. 122, 125.  $C_8H_{10}O$ . Calculated M. W. 122

3) Hexamethylbenzene (4.8 g.)..long needles m.p. 164-166°

(according to the literature - 166°)

Found M.W. 161, 165.  $C_{12}H_{18}$ . Calculated M.W. 162.

Gaseous reaction products contained 12.4%  $H_2$ , 32%  $CO_2$ , 10.8%  $CO$ ,  
9.2%  $C_nH_{2n}$ .

Alkylation at 420°. The initial mixture..305 g. of phenol, 623 g. of methyl alcohol. After the separation of the neutral products and unchanged phenol, 36 g. of a phenolic mixture were obtained with b.p. 182-224°. As a result of the fractionation of the mixture, two fractions were isolated in which was shown the presence of isomeric cresols. A fraction 189-191° (6 g.) contained the o-cresol. The melting point of the obtained arylglycolic acid was 151-152° (according to the literature - 152°). A fraction 200-203° (2.8 g.) contained m-cresol. The melting point of the arylglycolic acid was 100-103° which corresponds to the m.p. of m-cresoxyacetic acid (according to the literature - 103°).

The investigation of the neutral oil (128 g.) showed that it contained anisole (62 g.), o-methylanisole (7.5 g.) and hexamethylbenzene (7 g.).

Alkylation at 500°. The initial mixture..305 g. of phenol, 623 g. of methyl alcohol. After preliminary treatment of the condensate, 105.5 g. of a mixture of alkylated derivatives of phenol were obtained with b.p. 182-233° and 12 g. of phenols with b.p. above 233°. As a result of the analysis of the phenolic mixture, the presence of an insignificant amount of o-cresol was established (the m.p. of the obtained o-cresoxyacetic acid 151-152°) and of 3,5-dimethylphenol (the m.p. of the obtained arylglycolic acid - 84-86°).

A neutral oil (88 g.) contained anisole (28.5 g.), o-methylanisole (7 g.) and hexamethylbenzene (14.2 g.).

#### Conclusions

A mixture of methyl alcohol with phenol at 320-500° over a natural aluminosilicate catalyst - a gumbrin clay - forms alkylated derivatives of phenol and neutral products. O- and m-cresols and 3,5-dimethylphenol were isolated. The neutral reaction products contain anisole, o-methylanisole and hexamethylbenzene.

(References not revised)

From: Journal of General Chemistry 27, 2697-9 (1957)

The Catalytic Alkylation of Phenol  
with Methyl Alcohol

L. N. Samsonova

Translated from the Russian

by Paul W. Howerton

A series of works have been devoted to the catalytic alkylation of phenol with secondary and tertiary alcohols (1-8). Attempts at catalytic alkylation of phenol with primary alcohols led to negative results (2,3,9), or resulted in insignificant yields (10-13). For the alkylation of phenol with methyl alcohol, the best results were obtained on activated aluminum oxide (14).

We studied the process of the alkylation of phenol with methyl alcohol over an activated natural aluminosilicate catalyst - gumbrin clay - at atmospheric pressure in the usual apparatus used for investigation of vapor phase catalytic reactions in a circulating system. As a result of the reaction, liquid and gaseous products were obtained. The liquid, a two-layered condensate, besides unreacted starting materials, contained water, alkylated phenols and inert reaction products.

To determine the dependence of the yield of alkylated products on temperature, an accumulation of condensate for analysis was produced at three temperatures (350, 420 and 500°), at a mole ratio of phenol and methyl alcohol of 1:6 and rate of feed of the starting mixture equal to 8-10 ml. per hour over 100 ml. of catalyst. With an increase of reaction temperature from 350° to 500° the yield of alkylated phenols increased almost 3 times and reached 68% (based on the phenols of the condensate). The optimum yield of inert condensation products was obtained at 420° and amounted to 22% (based on the weight of the condensate).

The alkylated phenols obtained at the three investigated temperatures were a mixture of phenol derivatives containing cresols, xlenols and more complex products. The quantity of the latter increased markedly with increased reaction temperature. The mixture of alkylated phenols obtained at 350° contained 32% o-cresol. In the alkylation products obtained at 420°, the presence of o- and m-cresol was established. From the phenolic part of the condensate obtained at 500°, a small quantity of o-cresol and 3,5-dimethylphenol was isolated. The bulk of the phenols obtained at this temperature consisted of high-boiling complex alkylation products.

In the inert part of the condensates, besides alcohol and water, anisole, o-methylanisole and hexamethylbenzene were found. Anisole was obtained in greatest quantity at 420° (60.8% based on the inert oil). The maximum yield of hexamethylbenzene (14%) was obtained at 500°. The quantity of o-methylanisole in all cases was small.

#### Experimental Part

As a result of the catalytic condensation of phenol with methyl alcohol over hydrochloric acid activated gumbrin clay, two-layered condensates were obtained. The aqueous and oily layers were separated and a product boiling to 100° was distilled from each layer. The oily residue boiling above 100° was repeatedly extracted with 10% NaOH. The obtained phenolates were extracted with ether to free them from the slightly alkali-increased inert oil and washed with dilute H<sub>2</sub>SO<sub>4</sub>.

After drying of the ether solution and removal of the ether, a mixture of phenols was obtained which was then subjected to fractionation. At 182° the unreacted phenol was distilled off. The derivatives of phenol were fractionated on the column later. The phenols were analyzed by the method of

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arylation (15). The obtained crystalline arylglycolic acid was isolated by fractional crystallization.

In the course of the work it was established that after 18 hours of operation the catalyst lost almost 30% of its activity. Such deactivation of the catalyst is probably caused by deposits of oily residues and carbon on its surface, as a result of which the surface of the catalyst becomes inaccessible to the reacting substances. In all experiments after 6 hours of operation the catalyst was regenerated by blowing air at a temperature of  $350^{\circ}$  through the reaction tube. After 18 hours of operation a fresh portion of catalyst was placed in the reaction tube.

Freshly distilled, dried phenol and distilled methyl alcohol served as starting materials.

Alkylation at  $350^{\circ}$ . Starting mixture: 365.4 g. of phenol, 746 g. of methyl alcohol. After separation of the inert products and unreacted phenol, 38 g. of phenolic product with b. p.  $182-210^{\circ}$  and 159 g. of inert oil boiling in range of  $152-250^{\circ}$  were obtained. As a result of fractionation on a column, 11.5 g. of a fraction with b. p.  $187-189^{\circ}$  was isolated from the phenolic mixture. The arylglycolic acid obtained from part of the fraction after recrystallization had a m.p. of  $151-152^{\circ}$  which corresponds to the melting point of o-cresoxyacetic acid (according to the literature,  $152^{\circ}$ ).

From the inert oil there were isolated:

1) Anisole (48.5 g): b.p.  $155^{\circ}$ ,  $n_D^{20}$  1.5162,  $d_4^{20}$  0.9884.

Found: M.W. 108, 109.5.  $C_7H_8O$ . Calculated: M.W. 108

2) o-Methylanisole (11g): b.p.  $170-172^{\circ}$ ,  $n_D^{20}$  1.5190,  $d_4^{20}$  0.9850.

Found: M.W. 122, 125.  $C_8H_{10}O$ . Calculated: M.W. 122.



- 3) Hexamethylbenzene (4.8g) --- long needles, m.p. 164-166° (according to the literature, 166°).

Found: M.W. 161, 165.  $C_{12}H_{18}$ . Calculated: M.W. 162.

The gaseous products of the reaction contained 12.4%  $H_2$ , 32%  $CO_2$ , 10.8%  $CO$ , 9.2%  $C_nH_{2n}$ .

Alkylation at 420°. Starting mixture: 305 g. of phenol, 623 g. of methyl alcohol. After separation of the inert products and unreacted phenol, 36 g of a phenolic mixture with a b.p. of 182-224° was obtained. As a result of fractionation of the mixture, two fractions were isolated in which the presence of isomeric cresols was proven. The 189-191° fraction (6 g) contained o-cresol. The melting temperature of the obtained arylglycolic acid was 151-152° (according to the literature, 152°). The 200-203° fraction (2.8 g) contained m-cresol. The melting temperature of the arylglycolic acid was 100-103° which corresponds to the melting temperature of m-cresoxyacetic acid (according to the literature, 103°).

Investigation of the inert oil (128 g) indicated that it contained anisole (62 g), o-methylanisole (7.5 g) and hexamethylbenzene (7 g).

Alkylation at 500°. Starting mixture: 305 g of phenol, 623 g of methyl alcohol. After preliminary treatment of the condensate, 105.5 g of a mixture of alkylated derivatives of phenol with b.p. 182-233° and 12 g of phenols with b.p. above 233° were obtained. As a result of analysis of the phenolic mixture, the presence was established of a small quantity of o-cresol (melting temperature of obtained o-cresoxyacetic acid, 151-152°) and 3,5-dimethylphenol (melting temperature of obtained arylglycolic acid 84-86°).

The inert oil (88 g) contained anisole (28.5 g), o-methylanisole (7 g) and hexamethylbenzene (14.2 g).

### Conclusions

A mixture of methyl alcohol with phenol at 320-500° over a natural aluminate catalyst - gumbrin clay - produces alkylated derivatives of phenol and inert products. O- and m-cresol and 3,5-dimethylphenol were isolated. The inert products of the reaction contain anisole, o-methylanisole and hexamethylbenzene.

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